Anisotropic Thermal Conduction in a Polymer Liquid Subjected to Shear Flow

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Flow-induced anisotropic thermal conduction in a polymer liquid is studied using force Rayleigh scattering. Time-dependent measurements of the complete thermal diffusivity tensor, which includes one off-diagonal and three diagonal components, are reported on an entangled polymer melt subjected to a uniform shear deformation. These data, in conjunction with mechanical measurements of the stress, provide the first direct evidence that the thermal conductivity tensor and the stress tensor are linearly related in a deformed polymer liquid.

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Polymer flows, because they involve the dissipation of large amounts of energy, are inherently nonisothermal. Hence, the flow of polymer liquids involves a complex interaction of mechanical and thermal transport processes. Research in polymer dynamics has focused primarily on developing rheological models able to predict the stress in deforming polymers [1,2]. However, research on thermal transport in flowing polymers has received little attention [3].

A small body of theoretical work indicates that thermal conductivity is anisotropic in deforming polymer liquids [4–6]. For such systems, Fourier's law for the energy flux $\boldsymbol{q}$ is

$$\boldsymbol{q} = -\mathbf{k} \cdot \nabla T, \tag{1}$$

where T is the temperature field and $\mathbf{k}$ is the thermal conductivity tensor. Using a simple network model for polymer liquids, van den Brule [4] suggested that the thermal conductivity tensor and extra stress tensor $\boldsymbol{\tau}$ are linearly related:

$$\mathbf{k} - \tfrac{1}{3}\,\mathrm{tr}(\mathbf{k})\boldsymbol{\delta} = k_{\mathrm{eq}} C_t[\boldsymbol{\tau} - \tfrac{1}{3}\,\mathrm{tr}(\boldsymbol{\tau})], \tag{2}$$

where k_{eq} is the equilibrium thermal conductivity and C_t is the stress-thermal coefficient. The "stress-thermal rule" given in Eq. (2) is analogous to the well-known stress-optic rule relating the stress and refractive index tensors [7], which has been found to be valid for a large number of polymer liquids.

In a previous study, we reported the first quantitative measurements of anisotropic thermal conduction in a polymer liquid following a step shear deformation [8]. These results showed that thermal conduction was enhanced in the flow direction and decreased in the vorticity direction, relative to the equilibrium level. Measurements of the refractive index tensor (birefringence) in the same flow showed that anisotropy in the thermal and optical properties of a polymer liquid relaxed on the same time scale [8]. In a similar study on a cross-linked polymer subjected to simple elongation [9], we reported measurements of the thermal diffusivity tensor and tensile stress that provided direct evidence for the stress-thermal rule. Validity of the stress-thermal rule, Eq. (2), indicates that deformation-induced anisotropies in mechanical and thermal transport in polymers are governed by polymer chain orientation on a common length scale [8,9]. This observation could have profound implications on theoretical modeling because it provides guidance for the level of coarse graining necessary to describe anisotropic thermal conductivity. In addition, many of the results from molecular modeling of flow-induced polymer chain orientation can, if Eq. (2) is generally valid, be immediately used to develop semipredictive models.

In this Letter, we report the first measurements of the complete thermal diffusivity tensor in a polymer liquid subjected to a shear flow. The measurements are made using an improved version of the method used in our previous work that allows for more controlled deformations to be imposed and for more precise measurements of the thermal diffusivity. In addition, we report both birefringence and stress measurements in the same flow; the latter are used to directly assess the validity of the stress-thermal rule, Eq. (2).

The technique known as forced Rayleigh scattering (FRS) [10–12] was used to measure thermal diffusivity. Details of our FRS optical setup and the procedures used to measure thermal diffusivity are given elsewhere [10,12]. The FRS technique can be simply described as the creation (writing) of an optical grating within the sample and detecting (reading) its dynamics. The grating is written by the intersection of two beams from a coherent, high-power laser within a sample that contains a small amount of dye that absorbs the impinging light. The grating vector $\mathbf{g}$ lies in the plane formed by the two writing beams and is perpendicular to their direction of propagation. By a rapid, radiationless decay of the dye to its ground state, a sinusoidal temperature field with modulation amplitude δT and period $\Lambda = 2\pi/|\mathbf{g}|$ is created. Because the grating period Λ is much smaller than the spot size of the writing laser, the dynamics of the grating temperature field can be decoupled from the bulk temperature in the sample. Furthermore, if conditions for the plane grating approximation [10,12] are satisfied, δT following a pulse of writing laser is governed by

$$\rho C_p \frac{d}{dt}\delta T = -k_g g^2 \delta T, \tag{3}$$

where ρ is the mass density, C_p is the specific heat, and k_g is the thermal conductivity measured in the direction of the grating vector. The solution of Eq. (3) can be written as

$$\delta T \propto \exp(-t/\tau_g), \tag{4}$$

where the grating relaxation time is given by

$$\tau_g = \frac{\Lambda^2}{4\pi^2 D_g} \tag{5}$$

and where $D_g = k_g/\rho C_p$ is the thermal diffusivity in the grating direction. For typical organic liquids and grating sizes, the grating relaxation time $\tau_g \sim 10^{-3}$ s.

Through a rapid thermophysical process, the sinusoidally modulated temperature field creates a sinusoidally modulated density field with amplitude $\delta\rho$, which, in turn, creates a refractive index (phase) grating with amplitude δn. Now, since $c_0^2/g^2D_g^2 \ll 1$, where c_0 is the adiabatic speed of sound, and since $\tau_g \ll \tau_p$, where τ_p is the polymer relaxation time, $\delta\rho \propto \delta T$. Furthermore, since $\delta T \lesssim 10$ mK, $\delta n \propto \delta\rho$, so that from Eq. (4) we have $\delta n \propto \exp(-t/\tau_g)$. Dynamics of the grating were probed by a low-power reading laser introduced at the Bragg angle. A photodetector was used to measure the intensity of the first-order diffracted beam ($I_D \propto \delta n^2$) along with coherently ($\propto \sqrt{I_D}$) and incoherently scattered light producing a signal described by $V = A\exp(-2t/\tau_g) + B\exp(-t/\tau_g) + C$; the Levenberg-Marquardt method used to fit τ_g to V data is described elsewhere [12]. Consistency of the measured photodetector voltage with the biexponential function for V was carefully examined and interpreted as validation of the assumed thermophysical model [12].

The test fluid is a poly-isobutylene melt with a relatively narrow molecular weight distribution and a weight-average molecular weight of approximately 130 kDa. Dynamic mechanical measurements conducted at 25 °C were used to estimate the plateau modulus $G_N = 250$ kPa and mean relaxation time $\tau_p = 45$ s. Trace amounts of a dye (quinizarin), which absorbs at the writing laser wavelength but is nearly transparent at the reading laser wavelength, were uniformly dispersed within the polymer. An additional consistency check of the FRS method was made by making measurements at four grating sizes Λ in the range 25–75 μm and confirming the quadratic dependence of τ_g on Λ given in Eq. (5). Hence, all reported thermal diffusivities were obtained from at least four independent FRS experiments. All FRS experiments were conducted at a temperature of 298 ± 0.5 K. The equilibrium value of thermal diffusivity for the polymer liquid measured using FRS was found to be $D_{\mathrm{eq}} = (6.65 \pm 0.05) \times 10^{-4}$ cm^2/s.

A uniform shear deformation was imposed on the polymer in a planar Couette flow device. The polymer was loaded between the bases of two trapezoidal prisms separated by a nominal distance of 1 mm. One prism was stationary, and the other was driven by a computer-controlled stepper motor. If a shear strain γ, with x_1 as the flow direction and x_2 as the gradient direction, is applied to an incompressible viscoelastic fluid, then the state of stress in the fluid is given by the shear stress τ_{12}, and two normal stress differences $N_1 = \tau_{11} - \tau_{22}$ and $N_2 = \tau_{22} - \tau_{33}$ [1]. Since the strain is imposed in 80 ms $\ll \tau_p$, the flow is effectively a step strain deformation. For step strain flows of viscoelastic liquids, the following relationship between the shear stress and first normal stress difference has been shown to be valid: $N_1 = \gamma\tau_{12}$ [1]. Mechanical measurements of τ_{12} following step shear strain were made using a cone and plate rheometer.

Following a step strain, the prisms were aligned, creating multiple optical paths for the writing and reading laser beams. This allowed the grating vector to take four different orientations with respect to the coordinate system used to define the flow so that different projections of the thermal diffusivity tensor could be sampled with the FRS technique. The relationship between the thermal diffusivity measured along the grating direction D_g and the components of the thermal diffusivity tensor $D_{ij} = k_{ij}/\rho C_p$ in the shear flow coordinate system is given by

$$\begin{aligned} D_g = {} & D_{11}\cos^2(\alpha)\cos^2(\beta) + 2D_{12}\sin(\alpha)\cos(\alpha)\cos^2(\beta) \\ & + D_{22}\sin^2(\alpha)\cos^2(\beta) + D_{33}\sin^2(\beta), \end{aligned} \tag{6}$$

where α and β are angles between the grating vector and the x_1-x_3 and x_1-x_2 planes, respectively. In previous work [8] we were restricted to the case $\alpha = 0$ so that D_{11} was obtained with $\beta = 0$ and D_{33} with $\beta = \pi/2$. In the present study, we also consider the cases where $\beta = 0$ and $\alpha = \pm\pi/4$, allowing us to determine D_{22} and D_{12}.

The optical flow device was also used to measure the birefringence associated with flow-induced anisotropy of the refractive index tensor n [7]. Figure 1 shows that the ratio $(n_{11} - n_{22})/n_{12}$ for a strain $\gamma = 2.5$ is independent of time and equal to the applied strain. The inset showing the linear dependence of n_{12} on τ_{12} confirms the stress-optic rule yielding a stress-optic coefficient $C_0 = 3.07 \pm 0.03 \times 10^{-9}$ Pa^{-1} in good agreement with published values [7]. The data in Fig. 1, taken with the established result $N = \gamma\tau_{12}$, confirm that there is no slip between the polymer and glass surfaces for this strain. Measurements

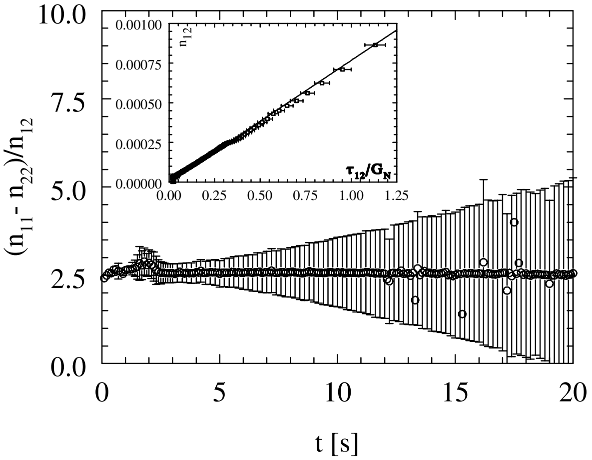

FIG. 1. Refractive index tensor components $(n_{11} - n_{22})/n_{12}$ versus time following a step strain $\gamma = 2.5$. The inset shows the birefringence n_{12} versus shear stress for the same flow confirming the stress-optic rule so that $(n_{11} - n_{22})/n_{12} = N_1/\tau_{12}$.

at larger strains were attempted, but it was not possible to rule out slip, consequently all reported experimental data are for a strain $\gamma = 2.5$.

Time-dependent values of thermal diffusivity following step strain in the flow direction D_{11} and the vorticity direction D_{33} are shown in Fig. 2. In the flow direction, the thermal diffusivity is increased above the equilibrium value by approximately 5% while a decrease of approximately 5% is observed in thermal diffusivity measured in the vorticity direction. At long times, both D_{11} and D_{33} appear to relax to the equilibrium value. These results are consistent with our previous study on a broad molecular weight distribution poly-isobutylene melt where it was possible to achieve larger strains and therefore larger deviations from equilibrium [8]. Figure 3 shows time-dependent values of D_{12} following a step strain. To our knowledge, these are the first reported measurements of an off-diagonal component of the thermal diffusivity (or conductivity) tensor. Immediately following the step strain, D_{12} is approximately 4% of D_{eq} and decays to zero at long times. Note that the error bars for D_{12} are somewhat larger than for D_{11} and D_{33} because D_{12} requires measurements at two grating orientations. We do not show data for D_{22}, which is similar to that shown in Fig. 3 for D_{33}.

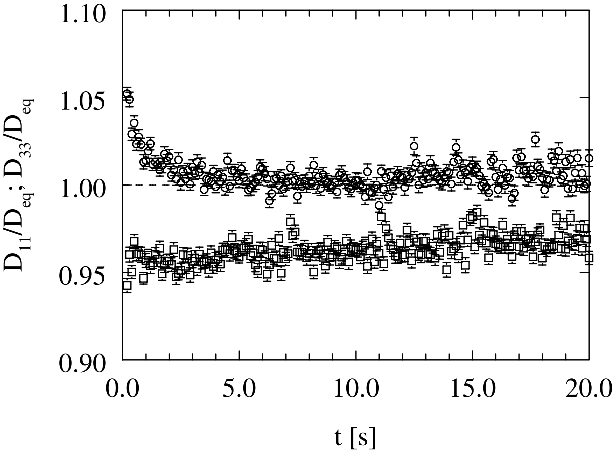

FIG. 2. Normalized thermal diffusivity tensor components in flow D_{11} (○) and vorticity D_{33} (□) directions versus time following a step strain $\gamma = 2.5$.

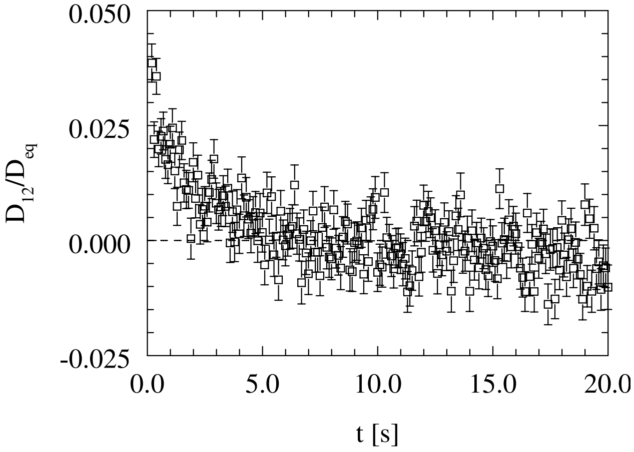

FIG. 3. Normalized thermal diffusivity tensor component in D_{12} (□) versus time following a step strain $\gamma = 2.5$.

Direct tests of the stress-thermal rule, Eq. (2), are made in Fig. 4. In Fig. 4(a), the off-diagonal component of the thermal diffusivity tensor D_{12} appears to be a linear function of the shear stress τ_{12}. A second test is shown in Fig. 4(b) where the difference between the components in the flow and gradient directions $D_{11} - D_{22}$ appears to be a linear function of the first normal stress difference

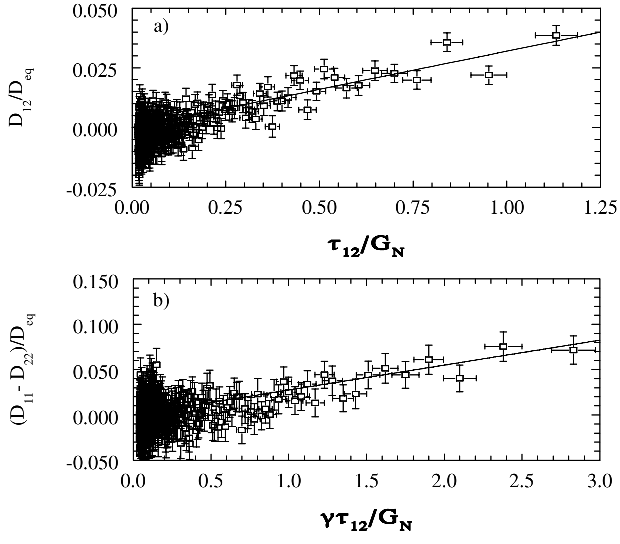

FIG. 4. Tests of the stress-thermal rule, Eq. (2), following a step strain $\gamma = 2.5$. (a) Linear dependence of D_{12} on τ_{12}. (b) Linear dependence of $D_{11} - D_{22}$ on $\gamma\tau_{12} = N_1$.

$N_1 = \tau_{11} - \tau_{22}$, which, as noted earlier, can be determined from $N_1 = \gamma\tau_{12}$. The data in Fig. 4 are the first direct evidence for validity of the stress-thermal rule in a deforming polymer liquid. The slopes of the lines in Fig. 4 can be used to determine the stress-thermal coefficient: (a) $C_t = 1.3 \pm 0.1 \times 10^{-7}\,\mathrm{Pa}^{-1}$; (b) $C_t = 1.1 \pm 0.1 \times 10^{-7}\,\mathrm{Pa}^{-1}$. These values are in good agreement with the estimate obtained in our previous study on a different poly-isobutylene liquid [8], and with the value $C_t = 1.3 \times 10^{-7}\,\mathrm{Pa}^{-1}$ found for a cross-linked vinyl methyl polysiloxane rubber in simple elongation [9].

It is interesting to note that similar C_t values have been found for two polymers with completely different chemistries: poly-isobutylene has a C-C backbone and poly-siloxane has a Si-O backbone. Recent results from molecular modeling suggest that anisotropic stress in polymer liquids is dominated by interchain forces [13]. The stress-thermal rule suggests that these same interchain forces also give rise to anisotropic thermal conduction. This picture suggests that conduction along a chain backbone is unimportant. Therefore, one might expect that nonassociating polymer liquids have similar values of the stress-thermal coefficient C_t.

In this Letter, we have presented further evidence that the stress-thermal rule is valid. In order for the stress-thermal rule to enjoy the same general validity as the stress-optic rule appears to have, it must be tested in other flows and for different polymer types. These studies will also shed further light on the possibly universal nature of flow-induced anisotropic thermal conduction in polymer liquids. Research on these areas is currently under way in our laboratory.

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